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RECENT RESULTS IN MUONIUM SOLUTION KINETICS

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Abstract

Using muonium spin rotation (MSR) techniques the aqueous solution
kinetics of several muonium addition reactions and spin conversion inter-
actions have been studied. The addition reactions show both diffusion
and activation-controlled reaction rates with isotope effects between 1
and 3 for diffusion-control and between 7 and 31 for activation-control
reactions. Barrier energies are typically ~15 kJ/mole and ~30 kJ/mole,
respectively, for these processes in water. Spin-conversion interactions
involving $Ni^{+2}_{(aq)}$ and $Ni(cyclam)^{+2}$ complexes showed that spin-conversion
of 'triplet' Mu by a paramagnetic solute occurs at or near the diffusion-
controlled limit while the chemical reaction with the diamagnetic con-
figuration of $Ni(cyclam)^{+2}$ occurred some 100 times slower at $k_M < 5 \times 10^{18}$
$M^{-1}s^{-1}$.

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Introduction

Since the first observation of muonium (Mu) in water [1] a number of water soluble inorganic and organic compounds [2] have been observed to undergo some form of chemical reaction with Mu. Several reaction types are possible (abstraction, addition, oxidation-reduction, substitution, acid-base, and spin-conversion) but we have focused here on addition reactions and spin-conversion interactions. With an emphasis on kinetic isotope effects, k_M/k_H, (where k_M and k_H are the Mu and H rate constants for a solute) the reaction kinetics of Mu addition reactions can be of use as a handle on H-atom reactions in general [2] and to the polymer industries as polymer initiation reaction rates in particular [3]. Furthermore the work with the nickel cyclam complex, fig. 1, (which can undergo an equilibrium configurational shift from the paramagnetic octahedral to diamagnetic square planar structure without changing its reduction potential, charge, or basic size [4,5]) shows the sensitivity of Mu as a probe for paramagnetism in solution [5].

Experimental

With the exception of cyanoacetate (98% pure) all the solutes studied were themselves Reagent-grade or were prepared from Reagent-grade compounds - as with $K_2Cd(CN)_4$.

This work was performed at TRIUMF's M20 channel using surface muons. Samples were held in shallow Teflon cells and bubbled continuously with high purity He to remove dissolved oxygen. Where necessary the pre-bubblers contained portions of the target solution to minimize reduction of the known solute concentration for volatile solutes. Room temperature cells were converted to temperature-controlled cells by the addition of a thermostated copper plate to the rear wall of the cell and the inclusion of a thermocouple to monitor the solution temperature. Transverse fields of ~8 G were used and λ_0 (for solute concentration [S] = 0) under these conditions was measured. Detailed descriptions of the experimental set up are available elsewhere [3,5].

Data histograms were computer analyzed with MINUIT to fit eq. (1) in order to evaluate the concentration dependent decay constant, λ.

$$N(t) = N_o exp(-t/\tau_\mu)[1 + A_D cos(\omega_D t + \phi_D) + A_M exp(-\lambda t)cos(\omega_M t - \phi_M)] + Bg \quad . \quad (1)$$

The chemical rate constants, k_M, were obtained from the slope of the best line from plots of λ vs. [S] to fit

$$\lambda = \lambda_o + k_M[S] \quad . \quad (2)$$

Rate data for temperatures between 273 and 353 K were evaluated with the Arrhenius equation to obtain pre-exponential and energy terms. To prove whether a reaction rate is diffusion controlled the data were plotted as k_M/T vs $1/\eta$, the inverse viscosity, because water structure and viscosity are both temperature dependent [2,6]. Straight line plots prove the reaction is indeed diffusion controlled [7].

Results

The room temperature values of k_M for maleic acid and acetone were taken from the literature [8] for comparative purposes. Table 1 lists the solutes studied; their addition reaction rate constants, k_M; their kinetic isotope effects, k_M/k_H; and those Arrhenius parameters evaluated. Muonium containing radicals have been observed in all the neat vinyl monomers listed [3,9] proving that addition of Mu to the double bond is taking place. For the cyanides muonium containing radicals were not observed but ESR data [10] show that both H and $\dot{O}H$ are capable of adding across the $C \equiv N$ bond.

Table 2 lists the data for paramagnetic and diamagnetic complexes of the nickel cyclam complex [5] as well as for aqueous Ni^{+2} [11].

Discussion

For addition reactions at the diffusion-controlled limit ($\sim 2 \times 10^{-10}$ $M^{-1}s^{-1}$) one would expect that the chemical rate constants k_M and k_H would be of the same magnitude since addition reactions are primarily electronic in nature. Though of similar magnitudes the resultant isotope effects, k_M/k_H, for the addition of Mu to C=C of maleic acid, acrylamide, acrylonitrile, and the C=O of quinone are equally divided between values near unity and three. Each value can be explained but exclusive of the other. If the mean thermal velocity of the adding

particle is important in diffusion one should observe an isotope effect of 3 because with a mass one ninth that of H, Mu's velocity is 3 times that of H [12]. On the other hand, if the Stokes-Einstein principle holds for both H and Mu there should be no velocity effect and the isotope effect should be unity. The tetracyanocadmate(II) $[Cd(CN)_4^{-2}]$ addition is diffusion controlled [7], but with k_H reported only as $>2.4\times10^9$ $M^{-1}s^{-1}$) [13] the k_M/k_H could be either 3 or 1. Without a temperature study on the isotope effect of 0.7 for Mu addition to CN^- itself cannot be added to the diffusion-controlled data.

As the reaction barrier energy increases above 15 kJ/mole, activation-control dominates and the rate constants get smaller. The isotope effect in these cases could be larger than 3 (the upper limit for diffusion-controlled isotope effects) because the lighter Mu atom should have a higher probability of 'tunneling' than H, but could be smaller if zero-point energy effects dominate. The isotope effects for benzoic acid, acetonitrile [7], cyanoacetate [7], and acetone [8] are all fairly large. Though quantum mechanical tunneling may be the reason for these large effects, not enough temperature data have been collected to correlate tunneling with the Arrhenius pre-exponential terms.

The electronic process of spin-conversion of "triplet" Mu with Ni^{+2} [11] and the paramagnetic $Ni(cyclam)^{+2}$ complexes [5] appear to be diffusion controlled. The chemical reaction of Mu with the diamagnetic $Ni(cyclam)^{+2}$ configuration, probably the abstraction of an H atom from a nitrogen or methylene group, is some 100 times slower. Because spin-conversion interactions of H are unobservable, isotope effects for these processes can not be evaluated.

Acknowledgements

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Table 1

Muonium Rate Constants at ~295 K, Isotope Effects, and Arrhenius
Parameters (E_a & A)

Solute	$k_M/M^{-1}s^{-1}$	k_M/k_H	E_a/kJ/mole	$A/M^{-1}s^{-1}$
Maleic acid	1.1×10^{10}	1.4	18.8	2.3×10^{13}
Acrylamide	1.9×10^{10}	1.1		
Acrylic acid	1.6×10^{10}			
Acrylonitrile	1.1×10^{10}	2.8		
Methylmethacrylate	1.0×10^{10}			
Styrene	1.1×10^{9}			
Acetonitrile	5.1×10^{7}	19		
Cyanoacetate	7.7×10^{7}	24	31	3.7×10^{13}
Cyanide	3.0×10^{9}	0.7		
Tetracyanocadmate(II)	1.7×10^{10}	<7	15	8.6×10^{12}
Benzoic acid	7.1×10^{9}	7.1		
Quinone	2.2×10^{10}	2.7		
Acetone	8.7×10^{7}	31		

Table 2

Muonium Spin-Conversion Rate Constants for Ni Ions

Solute	Spin	$k_M/M^{-1}s^{-1}$
Ni^{+2}	1	1.7×10^{10}
$Ni(cyclam)^{+2} \cdot 2H_2O$	1	4.5×10^{10}
$Ni(cyclam)^{+2} \cdot 2NH_3$	1	$\sim2.0 \times 10^{10}$
$Ni(cyclam)^{+2}$	0	$\leqslant5.0 \times 10^{8}$

Figure 1. Nickel cyclam configurations can undergo an equilibrium shift
by the addition of either an inert salt or ammonia. The cyclam macro-
cycle (1,4,8,11-tetraazacyclotetradecane) links the four coordinating
nitrogens by two and three carbon chains of methylene groups.

(Octahedral)   (Square Planar)

Paramagnetic (P)   Diamagnetic (D)